FORM INTO-1390 (Modified) (REV 11-98) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: **Muller-22**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR): **09/701054**

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/DE99/01898	**1 July 1999**	**3 July 1998**

TITLE OF INVENTION

Dealuminized Catalyst Support, Method for Producing Said Catalyst Support and Method for Hydrating C2- or C3-Olefins with Water in the Presence of a Catalyst Consisting of This Catalyst Support Impregnated with Acid

APPLICANT(S) FOR DO/EO/US

Michael Sakuth, Gregor Lohrengel, Dietrich Maschmeyer, and Guido Stochniol

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

Acknowledgment postcard
German application text as filed in PCT + 1 sheet of drawings + title page in English

534 Rec'd PCT/PTO 22 NOV 2000

U.S. APPLICATION NO. (IF KNOWN, SEE [illegible]) 09/701094	INTERNATIONAL APPLICATION NO. PCT/DE99/01898	ATTORNEY'S DOCKET NUMBER Muller-22

21. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

		CALCULATIONS PTO USE ONLY
☐	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO	**$1,000.00**
☒	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but Internation Search Report prepared by the EPO or JPO	**$860.00**
☐	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	**$710.00**
☐	International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)	**$690.00**
☐	International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)	**$100.00**
	ENTER APPROPRIATE BASIC FEE AMOUNT =	**$860.00**
	Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	35 - 20 =	15	x $18.00	**$270.00**
Independent claims	1 - 3 =	0	x $80.00	**$0.00**
Multiple Dependent Claims **(check if applicable)**.			☒	**$270.00**
	TOTAL OF ABOVE CALCULATIONS =			**$1,400.00**
☐	Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) **(check if applicable).**			**$0.00**
	SUBTOTAL =			**$1,400.00**
	Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +			**$0.00**
	TOTAL NATIONAL FEE =			**$1,400.00**
☐	Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).**			**$0.00**
	TOTAL FEES ENCLOSED =			**$1,400.00**
			Amount to be: refunded	$
			charged	$

☒ A check in the amount of **$1,400.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. in the amount of to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **02-4345** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

C. James Bushman
Browning Bushman
5718 Westheimer, Suite 1800
Houston, Texas 77057-5771
Tel.: (713) 266-5593
Fax: (713) 266-5169

SIGNATURE

C. James Bushman
NAME

24,810
REGISTRATION NUMBER

November 22, 2000
DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
ACTING AS RECEIVING OFFICE FOR THE PCT

In re Application of:		§	Attorney Docket No.: Muller-22
Michael Sakuth, Gregor Lohrengel, Dietrich Maschmeyer, and Guido Stochniol		§	
Int'l. Appln. No.:	PCT/DE99/01898	§	
Int'l. Filing Date:	1 July 1999	§	Art Unit No.: To Be Assigned
Priority Date:	3 July 1998	§	
U.S. Serial No.:	09/701,054	§	
U.S. Filing Date:	November 22, 2000	§	
For:	*Dealuminized Catalyst Support, Method for Producing Said Catalyst Support and Method for Hydrating C_2- or C_3- Olefins with Water in the Presence of a Catalyst Consisting of This Catalyst Support Impregnated with Acid* (as amended)	§	Examiner: To Be Assigned

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Attn.: DO/EO/US

Sir:

Kindly amend the above-identified application as follows:

In the Specification

Please delete the title in the English translation and substitute therefor the following title:

--Dealuminized Catalyst Support, Method for Producing Said Catalyst Support and Method for Hydrating C_2- or C_3-Olefins with Water in the Presence of a Catalyst Consisting of This Catalyst Support Impregnated with Acid--

On page 1, at line 9, insert the following subheadings:

--BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION--

On page 1, in line 12, delete "C_2 or C_3 olefins" and insert therefor --C_2- or C_3-olefins--.

On page 1, at line 15, insert the following subheading:

--DESCRIPTION OF THE PRIOR ART--

On page 1, in line 20, delete "therein".

On page 1, in line 27, delete "build" and insert therefor --made--.

On page 1, in line 28, delete "acid like for example" and insert therefor --acid, such as, for example,--.

On page 1, in line 30, delete "layer-lattice" and insert therefor "lattice-layer".

On page 2, in line 1, delete "for example those" and insert therefor --such as, for example, those--.

On page 2, in line 6, delete "catalysts like for example" and insert therefor --catalysts, such as, for example,--.

On page 2, delete lines 9-11 and substitute therefor --Until now, for carriers that are based exclusively on silicic acid in the form of silica gel, the mechanical hardness is questionable over a longer period of time--.

On page 2, in line 12, hyphenate the words "Aluminium" and "containing".

On page 2, in line 18, delete "apparatuess" and insert therefor --apparatuses--.

On page 2, in line 19, delete "thereby" and insert therefor --thus--.

On page 2, in line 25, insert a comma after the word "acid".

On page 2, in line 31, insert a comma after the word "aluminium".

On page 3, in line 1, delete "tetrachlorid" and insert therefor --tetrachloride--.

On page 3, in lines 2-3, insert a comma after the word "montmorillonite".

On page 3, after line 7, insert the following subheading and paragraphs:

--BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the rate of consumption of ethene versus reaction time using differently treated catalyst carriers; and

Figure 2 is a graph showing the rate of consumption of ethanol versus reaction time using differently treated catalyst carriers.--

On page 3, at line 8, insert the following subheading:

--SUMMARY OF THE INVENTION--

On page 3, in line 27, delete "at least one of the claims 1 to 22" and insert therefor --the present invention--.

On page 4, after line 24, insert the following subheading:

--DESCRIPTION OF THE PREFERRED EMBODIMENTS--

On page 3, in lines 10-11, delete "C_2 and C_3 olefins" and insert therefor --C_2- and C_3-olefins--.

On page 3, in line 18, insert a comma after the word "Surprisingly".

On page 3, in lines 20-21, delete the comma after "structure" and insert therefor --and--.

On page 3, in line 22, delete "have" and insert therefor --has--.

On page 3, in line 23 delete "C_2 and C_3 olefins" and insert therefor --C_2- and C_3-olefins--.

On page 3, in line 31, delete "Subject" and insert therefor --An object--.

On page 4, in line 5, delete "Further subject" and insert therefor --A further object--.

On page 4, in line 12, before the word "partial" delete "an" and insert therefor --a--.

On page 4, in line 17, delete "afterwardsrinsed" and insert therefor --afterwards rinsed--.

On page 4, in line 20, delete "Furthermore subject" and insert therefor --Yet another object--.

On page 4, in line 21 delete "C_2 or C_3 olefins" and insert therefor --C_2- or C_3-olefins--.

On page 4, in line 25, insert quotation marks around the words "hydration" and "hydration reaction".

On page 4, in lines 29-30, insert quotation marks around the words "dealuminating" and "dealuminated catalyst carrier".

On page 4, in line 30, insert a comma after "respectively".

On page 5, in line 1, insert the word --present-- before the word "invention" and insert a comma after the word "invention".

On page 5, in line 5, delete "cates," and insert therefor --and--.

On page 5, in line 6, delete "which" and insert therefor --that--.

On page 5, in line 6, delete "which" and insert therefor --that--.

On page 5, in line 12, delete "C_2 or C_3 olefins" and insert therefor --C_2- or C_3-olefins--.

On page 5, in line 14, insert a comma after the word "Thus".

On page 5, in line 23, delete the phrase "In particular preferred the" and insert therefor --In particular, a preferred--.

On page 5, in line 30, delete "are for example the" and insert therefor --are, for example, the--.

On page 5, in line 32, delete "components for example mica" and insert therefor --components, such as, for example, mica--.

On page 6, in line 2, insert the word "present" before the word "invention".

On page 6, in line 11, insert a comma after the word "acid".

On page 6, in lines 12-13, delete "in particular preferred" and insert therefor --more particularly,--.

On page 6, in line 30, delete "A example" and insert therefor --An example--.

On page 6, in line 31, insert the word "present" before the word "invention".

On page 7, in line 4, delete "silicates commercial" and insert therefor --silicates, commercial--.

On page 7, in line 6, hyphenate the words "bentonite" and "containing" and insert a comma after the word "carrier".

On page 7, in line 8, insert as comma after the word "as".

On page 7, in lines 9-11, delete the sentence "The catalyst carriers have preferably the form of spherical shapes, such as for example balls, lenses, cuboids, cylinders or also irregular forms, in particular preferred they have the shape of balls." and substitute therefore --The catalyst carriers preferably have the form of spherical shapes, such as, for example, balls, lenses, cuboids, cylinders or other irregular forms, and, most preferably, have the shape of balls.--

On page 7, in line 12, delete "preferred" and insert therefor --preferably--.

On page 7, in line 15, insert a comma after the word "carrier".

On page 7, in line 20, insert a comma after the word "acid".

On page 7, in line 23, insert a comma after the word "acid".

On page 7, in line 30, delete the phrase "like for example montmorillonite" and insert therefor --such as, for example, montmorillonite,--.

On page 7, in line 31, delete "Accompanying" and insert therefor --Accordingly,--.

On page 7, in line 32, delete the commas after the words "micropores" and "present".

On page 7, in line 33, delete "This" and insert therefor --These--.

On page 8, in line 10, insert a comma after "260°C".

On page 8, in lines 15-16, delete "solution and in particular preferred" and insert therefor --solution, most preferably".

On page 9, in line 5, insert a comma after the word "weight".

On page 9, in line 6, delete "C_2 or C_3 olefins" and insert therefor --C_2- or C_3-olefins--.

On page 9, in line 7, insert a comma after the word "carrier".

On page 9, in lines 6-8, delete the sentence "For impregnating the catalyst carrier preferably a 10 to 90% by weight phosphoric acid, most preferred a 30 to 60% by weight is used." and substitute therefor --For impregnating the catalyst carrier, preferably a 10 to 90% by weight, most preferably a 30 to 60% by weight, phosphoric acid is used--.

On page 9, in line 11, insert a comma after the word "catalyst".

On page 9, in line 14, insert a comma after "0.5".

On page 9, in line 18, insert a comma after the word "respectively".

On page 9, in line 22, delete "leads" and insert therefor --lead--.

On page 9, in line 34, delete "reprocesing for example distillative seperation" and insert therefor --reprocessing, such as, for example, distillative separation--.

On page 10, in line 3, insert a comma between the words "acid" and "it".

On page 10, in line 4, delete "the the" and insert therefor -the--.

On page 10, in line 7, delete "catalyst is it" and insert therefor --catalyst, it is--.

On page 10, in line 10, insert a comma after the word "discontinuously".

On page 10, in line 11, delete "reactor for example" and insert therefor --reactor, such as, for example,--.

On page 10, in lines 14-15, delete "afore mentioned" and insert therefor --aforementioned--.

On page 10, in line 25, insert a comma after the word "acid".

On page 10, in line 28, delete "in particular" and insert therefor --most preferably--.

On page 11, in line 9, delete the word "of".

On page 11, in lines 16-17, delete "preferably however" and insert therefor --more preferably--.

On page 11, in line 31, delete "C_2 or C_3 olefins" and insert therefor --C_2- or C_3-olefins--.

On page 12, in line 5, insert the word "most" before the word "preferably".

On page 12, in line 6, delete "shoul" and insert therefor --should--.

On page 12, in line 7, insert a comma after the word "weight".

On page 12, in line 9, insert a comma after the word "carrier".

On page 12, in line 12, insert a comma after the word "weight".

On page 12, in lines 15-16, insert a comma after the word "isothermally".

On page 12 in lines 21-22 delete "C_2 or C_3 olefin" and insert therefor --C_2- or C_3-olefin--.

On page 12, in lines 24-25, delete "using for example" and insert therefor --using, for example,--.

On page 12, in line 28, delete "temperature respectively it" and insert therefor --temperature, respectively, it--.

On page 13, in line 15, delete "out by for example" and insert therefor --out, such as, for example, by--.

On page 13, in line 17, insert a comma after the word "catalyst".

On page 13, in lines 21-22, delete "reactor for example" and insert therefor --reactor, such as, for example,--.

On page 13, in line 16, delete "during in" and insert therefor --during--.

On page 13, in line 23, delete "refer result" and insert therefor --refer to results--.

On page 13, deletes lines 29-33.

On page 15, in line 19, delete "is" and insert therefor --being--.

On page 15, in line 15, delete "is employed ('old carrier') and insert therefor --was employed ("old carrier")--.

On page 17, in line 31, delete "('old carrier')" and insert therefor --("old carrier")--.

Renumber pages 1-8 following page 20 to pages 21-28, respectively.

On the page numbered 8 following page 20, delete lines 1-5 and substitute therefor the following subheading:

--ABSTRACT--

On the page numbered 8 following page 20, in line 10, delete "as for example" and insert therefor --as, for example,--.

On the page numbered 8 following page 20, in lines 11-12, delete "C_2 or C_3 olefins" and insert therefor --C_2- or C_3-olefins--.

On the page numbered 8 following page 20, incorporate the paragraph beginning at line 16 into the preceding paragraph ending at line 15.

On the page numbered 8 following page 20, in lines 20-21, delete "apparatusdue to aluminium phosphate are expected" and insert therefor --apparatus due to aluminium phosphate is expected--.

In the Claims

Please cancel Claims 1-35 and substitute the following new claims, 36-74:

--36. A catalyst carrier comprising a lattice-layer silicate having an aluminium content of less than 0.3% by weight.

37. The catalyst carrier according to Claim 36 wherein the aluminium content is less than 0.03% by weight.

38. The catalyst carrier according to any one of Claims 36 or 37 wherein said lattice layer silicate is a smectite.

39. The catalyst carrier according to any one of Claims 36 or 37 wherein said lattice-layer silicate has a montmorillonite structure.

40. The catalyst carrier according to any one of Claims 36 or 37 wherein the cumulative pore volume is between 0.2 and 0.9 ml/g.

41. The catalyst carrier according to Claim 40 wherein the cumulative pore volume is between 0.6 and 0.7 ml/g.

42. The catalyst carrier according to any one of Claims 36 or 37 in the shape of a spherical body.

43. The catalyst carrier according to Claim 42 wherein said spherical body comprises a ball.

44. The catalyst carrier according to Claim 42 wherein said spherical body has a diameter of between 1 and 10 mm.

45. The catalyst carrier according to Claim 44 wherein said spherical body has a diameter of between 4 and 6 mm.

46. The catalyst carrier according to any one of Claims 36 or 37 wherein the pressure resistance is at least 10 N/mm.

47. The catalyst carrier according to Claim 46 wherein the pressure resistance is at least 20 N/mm.

48. A method of producing a catalyst carrier containing less than 0.3% by weight aluminium comprising impregnating a lattice-layer silicate with an acid, hydrothermally treating the acid-impregnated lattice-layer silicate, and washing the hydrothermally treated, acid-impregnated, lattice-layer silicate with a wash solution selected from the group consisting of acidic solutions, basic solutions, or neutral solutions.

49. The process according to Claim 48 wherein said neutral solution is water.

50. The process according to any one of Claims 48 or 49 wherein said acid comprises a mineral acid.

51. The process according to Claim 50 wherein said mineral acid comprises phosphoric acid.

52. The process according to any one of Claims 48 or 49 wherein said hydrothermal treatment is conducted at a temperature of between 160 and 300°C and a partial water vapor pressure of between 4 and 80 bar_{abs}.

53. The catalyst carrier according to Claim 51 wherein said hydrothermal treatment is conducted at a temperature of between 220 and 260°C and a partial water vapor pressure of between 16 and 25 bar_{abs}.

54. The catalyst carrier of any one of Claims 48 or 49 wherein said hydrothermal treatment is conducted, at least in part, during the use of said catalyst carrier in a hydration reaction.

55. The process according to any one of Claims 48 or 49 wherein said washing takes place at a temperature of between 20 and 100°C.

56. The process according to Claim 55 wherein said washing takes place at a temperature of between 70 and 90°C.

57. The process according to any one of Claims 48 or 49 wherein said washing solution comprises hydrochloric acid.

58. The process according to any one of Claims 48 or 49 wherein the washed, hydrothermally treated, acid-impregnated, lattice-layer silicate is rinsed with water.

59. The process according to any one of Claims 48 or 49 wherein said washing solution comprises water containing up to 30 parts of concentrated hydrochloric acid.

60. The process according to Claim 58 wherein said rinsing is conducted until the rinsing water is neutral.

61. The process according to any one of Claims 48 or 49 wherein said lattice-layer silicate is purified by burning off adhering organic carbon-containing compounds at a temperature of between 300 and 1000°C prior to any of the steps set forth in Claim 48.

62. A catalyst carrier produced by the process according to any one of Claims 48 or 49.

63. A process for hydrating an olefin with water in the presence of at least one catalyst made from the catalyst carrier according to any one of Claims 48 or 49.

64. The process according to Claim 63 wherein said catalyst contains from 5 to 60% by weight of acid and the hydration is carried out in a reactor with an olefin to water molar ratio of from 0.1 to 0.8, at a gas hourly space velocity of 10 to 100 $l_n/min/1_{cat}$ at a temperature of between 160 and 300°C and a pressure of between 20 and 200 bar_{abs}.

65. The process according to any one of Claims 63 or 64 wherein said acid is phosphoric acid.

66. The process according to Claim 65 wherein said phosphoric acid is present in an amount of from 10 to 90% by weight.

67. The process according to Claim 66 wherein said phosphoric acid is present in an amount of from 50 to 60% by weight.

68. The process according to any one of Claims 63 or 64 wherein the hydration reaction is carried out at a temperature of between 220 and 260°C and a pressure of between 60 and 80 bar_{abs}.

69. The process according to any one of Claims 63 or 64 wherein the olefin and said water are present in gaseous form.

70. The process according to any one of Claims 63 or 64 wherein said olefin is a C_2-olefin, a C_3-olefin, or a mixture thereof.

71. The process according to Claim 64 wherein said acid is introduced during the hydration reaction.

72. The process according to Claim 70 wherein said acid comprises phosphoric acid.

73. The process according to Claim 64 wherein acid is continuously injected during the hydration reaction.

74. A catalyst carrier according to any one of Claims 48 or 49 having at least partially a cristobalite-like structure.--

Respectfully submitted,

C. James Bushman
Reg. No. 24,810

Date: 12/15/00

Browning Bushman
5718 Westheimer, Suite 1800
Houston, TX 77057
Tel.: (713) 266-5593
Fax: (713) 266-5169

CERTIFICATE OF EXPRESS MAILING

I, Jan C. Lipscomb, hereby certify that this correspondence and all referenced enclosures are being deposited by me with the United States Postal Service as Express Mail with Receipt No. EL010850979US in an envelope addressed to Box PCT, Assistant Commissioner for Patents, Washington, DC 20231, on December 15, 2000.

By: Jan C. Lipscomb

Dealuminated catalyst carrier, process for producing the catalyst carrier and process for hydrating C_2 or C_3 olefins with water in the presence of a catalyst which consists this catalyst carrier impregnated with acid.

Claimed is a dealuminated catalyst carrier, a process for producing the catalyst carrier and a process for hydrating C_2 or C_3 olefins with water in the presence of a catalyst which comprises this catalyst carrier impregnated with acid.

It is known that olefins of low molecular mass which are linear or have only few branches can be converted to alcohols by a reaction with steam in the gas phase under the application of high temperatures and pressures. Of significance for large scale is therein the synthesis of ethanol from ethene and of isopropanol from propene. The production of these alcohols takes place in the presence of acidic catalysts, wherein usually a catalyst carrier consisting of an alumosilicate and a silicate material is used, which has been impregnated with phosphoric acid, respectively.

The material of the catalyst carrier is usually build up of pure silicic acid like for example silica gel (US 2,579,601) or consists of silicic acid with a varying amount of alumina (US Patent No. 3,311,568) and consists of pure layer-lattice silicates (sheet-

structure silicates), for example those containing montmorillonite (DE 29 08 491), respectively.

Apart from these phosphoric acid-containing catalyst carriers, also zeolithic materials are used (EP 0 323 269 B1) or other acidic catalysts like for example zircon phosphate (GB 00 55 34).

Until now for carriers which are based on silicic acid in the form of silica gel exclusively the mechanical hardness is questionable over a longer hold up time. Aluminium containing catalyst carriers or those consisting of only alumina show a noticeably higher long-term stability, but they have the immense disadvantage that aluminium is leached out from the catalyst carrier during the hydration reaction due to the effect of phosphoric acid. The aluminium ends up in the succeeding apparatuess as poorly soluble sedimentations in form of aluminium phosphate. These apparatuses thereby are gradually blocked.

In DE 1 156 772 a process is described for reducing the aluminium content of the lattice-layer silicate by reaction with hydrochloric acid. However, even after intensive washing with hydrochloric acid the carrier material still shows the presence of approximately 1 to 2 % by weight of aluminium.

In EP 0 578 441 B1 by using a pelletised silicate carrier based on aerosil (Degussa) which does not contain aluminium a certain long-term stability is achieved. Starting material for the production of aerosil is the

relatively expensive silicon tetrachlorid. Since materials based on lattice-layer silicates, such as montmorillonite for example, are natural raw materials which can be excavated from relevant deposits in the earth, these have an obvious advantage over pelletised silicate carriers according to the economic efficiency of the hydrating process.

The present invention is based on the problem of finding an economical process for the hydration of C_2 and C_3 olefins with water in the presence of a catalyst which comprises a catalyst carrier impregnated with acid and in which the catalyst carrier has a long term stability as high as possible and simultaneously the leaching out of aluminium during the hydration reaction is as little as possible.

Surprisingly it has been found that a dealuminated catalyst carrier based on mainly aluminium-containing lattice-layer silicates with a montmorillonite structure, an aluminium content of less than 0.3% by weight have a high long-term stability, and that during the process of hydrating C_2 or C_3 olefins with water in the presence of a catalyst which comprises a catalyst carrier impregnated with acid, by carrying out the hydration reaction using a dealuminated catalyst carrier according to at least one of the claims 1 to 22, no or only very small amounts of aluminium are washed out of the catalyst carrier.

Subject of the present invention is therefore a dealuminated catalyst carrier based on mainly aluminium-containing lattice-layer silicates with a montmorillo-

nite structure with an aluminium content of less than 0.3 % by weight. Preferred forms of the catalyst and of the process are described in the sub-claims.

Further subject of the present invention is a process for the reduction of the aluminium content of a catalyst carrier which comprises mainly aluminium-containing lattice-layer silicates with a montmorillonite structure, wherein the catalyst carrier is

- impregnated with phosphoric acid
- treated hydrothermally at a temperature of between 160 and 300 °C and an partial water vapour pressure of 4 to 80 $bar_{absolute}$
- washed subsequently with an acidic, basic or neutral solution at a temperature of between 20 and 100 °C, and
- afterwardsrinsed with water until the washing water becomes neutral.

Furthermore subject of the present invention is a process for the hydration of C_2 or C_3 olefins with water in the presence of a catalyst that comprises a catalyst carrier impregnated with acid according to at least one of the claims 1 to 22.

The terms hydration and hydration reaction refer, for the purposes of this invention, to the reaction of water with a carbon-carbon double bond.

The terms dealuminating and dealuminated catalyst carrier, respectively refer for the purposes of this invention to the process of reducing the aluminium content and a catalyst carrier with a reduced aluminium content.

By carrying out the process according to the invention a catalyst carrier can be produced which is based on calcined and subsequently treated lattice-layer silicates, that has a noticeably reduced aluminium content compared to a catalyst carrier which has not been treated according to this invention. In spite of the reduced aluminium content, the long-term stability of the catalyst has been maintained. By using a catalyst carrier according to this invention during the process also according to this invention for the hydration of C_2 or C_3 olefins with water, the amount of aluminium leaching out during the hydration reaction is noticeably reduced. Thus fewer insoluble aluminium compounds are produced during the hydration reaction, which in conventional processes lower the hold up time of the succeeding apparatuses, such as heat exchangers, by blocking the pipes or the areas of heat exchange.

The dealuminized catalyst carrier according to this invention with an aluminium content of less than 0.3 % by weight contains mainly aluminium-containing lattice-layer silicates. In particular preferred the dealuminized catalyst carrier according to this invention has an aluminium content of less than 0.03 % by weight. The aluminium-containing lattice-layer silicates are preferably smectites and have preferably montmorillonite structures. Lattice-layer silicates which exhibit mainly aluminium-containing lattice-layer silicates with montmorillonite structures are for example the bentonites. Apart from the montmorillonites, bentonites can contain other components for example mica, illite, crystobalite and zeolite.

Starting material for the production of a catalyst carrier according to the invention are conventional catalyst carriers for examples based on calcined and subsequently treated lattice-layer silicates.

The dealuminized catalyst carrier according to this invention with an aluminium content of less than 0.3 % by weight, preferably less than 0.03 % by weight, based on mainly aluminium rich lattice-layer silicates with a montmorillonite structure can be made by impregnating the catalyst carrier with phosphoric acid preferably a 10 to 90 % by weight phosphoric acid, in particular preferred a phosphoric acid of 50 to 60 % by weight so that the catalyst carrier contains between 5 and 60 %, preferably between 30 and 40 % phosphoric acid, followed by hydrothermal treatment at a temperature of between 160 and 300 °C, preferably at a temperature of between 220 and 260 °C and a partial water vapour pressure of between 4 and 80 $bar_{absolute}$, preferably at a partial water vapour pressure of between 16 and 25 $bar_{absolute}$, followed by washing with an acidic, basic or neutral solution, preferably an acidic or neutral solution, in particular with water, hydrochloric acid or water containing 0 to 30 parts concentrated hydrochloric acid at a temperature of between 20 and 100 °C, preferably of between 70 and 90 °C and afterwards rinsing the catalyst carrier until the washing water has become neutral.

A example of how to carry out the process according to the invention for reducing the aluminium content of a catalyst carrier is described below, without limiting the process of the present invention to this example.

For the reduction of the aluminium content of a catalyst carrier which comprises mostly aluminium-containing lattice-layer silicates, commercial lattice-layer silicates such as, for example, montmorillonite or bentonite-containing catalyst carriers can be used. The catalyst carriers have preferably the form of spherical shapes, such as for example balls, lenses, cuboids, cylinders or also irregular forms, in particular preferred they have the shape of balls. The spherical shapes have preferably an average diameter of 1 to 10 mm, most preferred a diameter of 4 to 6 mm.

For the reduction of the aluminium content in the catalyst carrier it is impregnated with acid, treated hydrothermally, subsequently washed and afterwards rinsed.

The catalyst carrier is impregnated with acid, preferably phosphoric acid in order to produce the effect according to the invention. A 10 to 90 % by weight phosphoric acid, preferably a 50 to 60 % by weight phosphoric acid is used. After being impregnated, the catalyst carrier should show an amount of phosphoric acid of 5 to 60 % by weight, preferably 30 to 40 % by weight. Afterwards the catalyst carrier is treated hydrothermally.

Under the hydrothermal conditions the lattice-layer silicate material, like for example montmorillonite changes into cristobalite-like structures. Accompanying the micropores, that were previously present, disappear. This morphological changes in structure can

clearly be seen by the BET surface, the pore volume and the distribution of pore radii. Under hydrothermal reaction conditions the so-called "open" pore structures are attained.

Hydrothermal treatment of the catalyst carrier containing lattice-layer silicates can be carried out at temperatures of between 160 and 300 °C under a partial water vapour pressure of between 4 and 80 $bar_{absolute}$, preferably between 220 and 260 °C and a partial water vapour pressure of between 16 and 25 $bar_{absolute}$.

After hydrothermal treatment the catalyst carrier is washed with a basic, acidic or neutral solution, preferably with an acidic or neutral solution and in particular preferred with hydrochloric acid, with water containing 0 to 30 parts concentrated hydrochloric acid or with a neutral aqueous solution. The washing of the catalyst carrier is carried out at a temperature of between 20 and 100 °C, preferably between 70 and 90 °C.

After said washing the catalyst carrier can be rinsed with water until the washing water used to rinse becomes neutral.

The catalyst carrier then has a cumulated pore volume of between 0.2 and 0.9 ml/g, preferably between 0.6 and 0.7 ml/g. The pressure resistance of the catalyst carrier should be of at least 10 N/mm, preferably at least 20 N/mm.

In a specific embodiment of the process according to the invention, the hydrothermal treatment of the catalyst carrier impregnated with acid, which contains 5 to 60 % by weight phosphoric acid, preferably 30 to 40 % by weight takes place by use as a catalyst in a hydration reaction of C_2 or C_3 olefins. For impregnating the catalyst carrier preferably a 10 to 90 % by weight phosphoric acid, most preferred a 30 to 60 % by weight is used.

During this hydration in a reactor filled with catalyst preferably a tubular reactor olefin and water in a molar ratio of between 0.1 and 0.8, preferably between 0.15 and 0.5 are reacted. The olefin to be used and the water to be used are introduced into the reactor gaseous or liquid, preferably gaseous. For evaporating the water and heating both reagents to reaction temperature, respectively it may be beneficial to introduce both reagents into the reactor over a vaporisation or thermostat-controlled section, which is heated to the reaction temperature electrically or by way of heat carriers which leads into the reactor. The gas hourly space velocity (GHSV) should be between 10 and 100 $l_n/min/l_{cat}$. The hydration reaction is carried out at a temperature of between 160 and 300 °C and an absolute pressure of between 20 and 200 bar. The hydration of ethene to ethanol is carried out preferably at a temperature of between 220 and 260 °C and an absolute pressure of between 60 and 80 bar.

The exit of the reactor can prferably be connected to a cooler which condenses out the majority of the subcritical components and makes them accessible to further reprocesing for example distillative seperation.

For controlling the activity and selectivity of the catalyst carrier impregnated with acid it can be advantageous to analyse the the outflow of the reactor. The analysis can be carried out by gas chromatography.

To increase the lifetime of the catalyst is it advantageous to add the acid, with which the catalyst carrier has been impregnated, into the reactor continuously or discontinuously preferably continuously. The acid can be introduced into the reactor for example by injection. The amount of acid which is introduced into the reactor can be made dependent on the results of the analysis of the outflow. Both the analysis of the afore mentioned energy released from the reaction, as well as the resulting amount of acid to be introduced can be carried out by automation.

After the hydrothermal treatment of the catalyst carrier by being used as a catalyst in a hydration reaction, the remaining acid with which the catalyst carrier has been impregnated is removed by washing with water until the washing water becomes neutral.

After the removal of the remaining acid the catalyst carrier is washed with a basic, acidic or neutral solution, preferably with an acidic or neutral solution and in particular preferably with hydrochloric acid, with water which contains 0 to 30 parts concentrated hydrochloric acid or a neutral aqueous solution. The catalyst carrier can be washed at a temperature of between 20 and 100 °C, preferably at a temperature of between 70 and 90 °C.

After the washing the catalyst carrier can be rinsed with water until the washing water becomes neutral.

In the case of catalyst carriers which by being used as catalysts in a hydration reaction have been hydrothermally treated, it may be advantageous, after reducing the aluminium content in the catalyst carrier, to clean of the catalyst carrier by burning off possible carbon compounds attached at between 300 and 1,000 °C, preferably between 450 and 500 °C.

Both variations of the process according to this invention result in a treated catalyst carrier with a reduced aluminium content. The treated catalyst carriers have an average diameter of between 1 and 10 mm, preferably however of between 4 and 6 mm. The total pore volume is between 0.2 and 0.9 ml/g, preferably between 0.6 and 0.7 ml/g. The pressure resistance after the treatment of the catalyst carrier is at least 10 N/mm, preferably 20 N/mm. The amount of aluminium in the treated catalyst carriers is less than 0.3 % by weight, preferably less than 0.03 % by weight.

The catalyst carriers produced by the process according to this invention with reduced aluminium content can be used for the production of catalysts.

The catalyst carriers produced by the process according to this invention with a reduced aluminium content can according to the invention be used for the hydration of C_2 or C_3 olefins with water in the presence of a catalyst, which consists mainly of a catalyst carrier

treated according to the invention having been impregnated with acid.

Preferably the catalyst carrier is impregnated with an acid, preferably phosphoric acid. The quantity of phosphoric acid shoul be between 5 and 60 % by weight, preferably between 30 and 40% by weight to obtain the maximum catalytic activity of the impregnated catalyst carrier. For impregnating the catalyst carrier an aqueous phosphoric acid solution which contains a phosphoric acid quantity of between 10 to 90 % by weight, preferably between 50 and 60 % by weight is used. The acidic catalyst thus produced is filled in a reactor, preferably a tubular reactor. The reactor is operated isothermally or non-isothermally, preferably isothermally and can be heated electronically or by way of heat carriers.

The reactor is fed continuously or discontinuously, preferably continuously, with the reagents water and C_2 or C_3 olefin. The ratio of water to olefin with which the reagents are fed into the reactor is adjusted at a molar ratio of between 0.1 to 0.8, preferably between 0.15 and 0.5 . The molar ratio can be adjusted by using for example a mass flowmeter. Both reagents can be introduced into the reactor liquid or gaseous, preferably gaseous. For evaporating the water and heating both reagents to reaction temperature respectively it may be beneficial to introduce both reagents into the reactor over a vaporisation or thermostat-controlled section, which is heated to the reaction temperature electrically or by way of heat carriers. The temperature in the reactor and the temperature with which the reagents flow into the reactor should be between 160 and 300 °C.

For the hydration reaction of ethene to ethanol, the temperature in the reactor and the temperature with which the reagents flow into the reactor is preferably between 220 and 260 °C. The pressure in the reactor is in the range of between 20 and 200 $bar_{absolute}$, preferably between 60 and 80 $bar_{absolute}$.

The exit of the reactor is preferably connected to a cooler, which can condense out the majority of the components and make these accessible to further reprocessing.

To control the activity and selectivity of the acid impregnated catalyst carrier, it can be beneficial to analyse the outflow of the reactor. This analysis can be carried out by for example gas chromatography.

To increase the lifetime of the catalyst it is advantageous to add the acid, preferably phosphoric acid, with which the catalyst carrier has been impregnated, into the reactor continuously or discontinuously, preferably continuously. The acid can be introduced into the reactor for example by injection. The amount of acid which is introduced into the reactor can be made dependent on the results of the analysis of the outflow. Both the analysis of the outflow and the determination resulting amount of acid to be introduced can be carried out by automation.

Figure 1 and Figure 2 show the rate of consumption of ethene and the rate of formation of ethanol in dependence of the reaction time by using differently treated catalyst carriers without limiting the process according to this invention to these results.

Figure 1

In figure 1 the rate of consumption of ethene during a hydration reaction is shown in dependence of the reaction time. The data from four experiments are shown. The measurements represented by circles refer to the rate of consumption of ethene relative to reaction time when a new catalyst carrier containing the original amount of aluminium is used. The data of the rate of consumption of ethene represented by squares result from three series of experiments which were carried out using a catalyst carrier with a reduced aluminium content.

Figure 2

In figure 2 the rate of formation of ethanol during in a hydration reaction in dependence of the reaction time is shown. The data from four experiments are shown. The measurements represented by circles refer to the rate of formation of ethanol relative to reaction time when a new catalyst carrier containing the original amount of aluminium is used. The data of the rate of formation of ethanol represented by squares refer result from three series of experiments which were carried out using a catalyst carrier with a reduced aluminium content.

The process according to the present invention is described by the examples below without being limited to these examples.

Example 1: The synthesis of ethanol with an untreated catalyst carrier

The experiment took place in a pilot plant whose core part contains an isothermally operated tubular reactor of 1,000 mm in length and 48 mm diameter.

The reagents water and ethene are introduced into the reactor over a vaporisation or thermostat-controlled section, which is electrically heated to the reaction temperature. The water is introduced liquidly through a pump, while ethene is taken from a 130 bar steel flask. The introduction of a mixture of ethene : water at a molar ratio of 0.3 : 1 is controlled by a mass flow-meter.

The exit of the reactor is connected to a cooler which condenses out the majority of the subcritical components, mainly ethanol, water and diethylether, the rest is diverted to the waste gas whose volumetric flow is measured by a gas-meter. A part of the waste gas is fed through a bypass into a gas chromatograph. The liquid products are also analysed by gas chromatography.

The synthesis of ethanol according to the present example was measured at a temperature of 240 °C and a pressure of 70 $bar_{absolute}$. The standard test conditions are summarised in Table 1. The catalyst used was an untreated new catalyst carrier, the KA-1 of Südchemie AG. The properties of the carrier are summarised in Table 2. Conversion and selectivity values reached at the start of the experiment are included in Table 2.

To determine the aluminium content of the catalyst carrier this was analysed with an atomic emission spectrometer before the start of an experiment. The atomic emission spectrometer used was an inductively coupled plasma atomic emission spectrometer (ICP-AES) JY 38+ made by ISA Jobin Y. The results of the analysis are shown in Table 2.

Example 2: The synthesis of ethanol with an untreated old carrier

The experiment was repeated in the same way as described in Example 1. This time an untreated catalyst carrier that had already been used for the catalysis of a hydration reaction is employed ('old carrier'). Again the standard test conditions shown in Table 1 are relevant. The results of the experiment as well as the properties of the catalyst carrier are given in Table 2.

As can be seen from the values in Table 2, the specific surface of the impregnated catalyst carrier decreases after the catalyst has been used only once. Similarly the aluminium content is reduced to approximately ¼ of its original value by the single use as catalyst. The remaining ¾ of the original amount of aluminium in the untreated new carrier are leached out during the hydration reaction. This aluminium forms the insoluble sedimentations which hinders the reprocessing steps.

Example 3: The synthesis of ethanol with a treated old carrier

The experiment was carried out in the same way as described in Example 1. As catalyst carrier an already used old carrier was employed whose aluminium content had been reduced by treatment according to the process of this invention. Again the standard test conditions shown in Table 1 are relevant. The results of the experiment as well as the properties of the catalyst carrier are also given in Table 2.

The deactivation of the catalyst carrier with, as well as without, a reduced aluminium content are represented in both Figure 1 and Figure 2.

As can be seen from Table 2 the aluminium content of a catalyst carrier is reduced to less than 0.03 % by weight by treating the old carrier in the process according to this invention. This value represents the detection limit of the atomic emission spectrometer used. The pressure resistance of the treated old carrier is 30 N/mm sufficient to guarantee good long-term stability of the catalyst carrier.

In spite of treating the catalyst carrier and reducing its aluminium content to a value less than 0.03 % by weight, the conversion of ethylene and the yield of ethanol both remained good compared to an untreated, unused catalyst carrier ('new carrier') and to an un-

treated old carrier, respectively, even slightly increased in the present example.

As can be seen from Figure 1 and Figure 2 reducing the aluminium content according to the process of the invention has no influence on the rate of consumption of ethene nor on the rate of formation of ethanol.

Standard experimental conditions	
Process Parameter	*Value*
total reaction pressure	70 bar
temperature of the reactor (isotherm)	240°C
GHSV	21.3 $l_n/min/l_{cat}$
water : ethene	1.0 : 0.3 mol : mol
carrier material	KA-1 (Südchemie)

Table 1: The standard experimental conditions used in all experiments.

Property (impregnated carrier)	*New Carrier*	*Untreated Old Carrier*	*Treated Old Carrier*
force withstood	20 N/mm	40 N/mm	30 N/mm
spec. surface (BET)	20 m^2/g	4 m^2/g	3 m^2/g
cumulated pore volume	0.7 ml/g	0.4 ml/g	0.4 ml/g
Al content	1.3 % b.w.	0.31 % b.w.	< 0.03 % b.w.
Si content	25 % b.w.	25 % b.w.	24 % b.w.
H_2PO_4 content	35 % b.w.	36 % b.w.	35 % b.w.
ethene turnover at start of experiment	5 %	5 %	6 %
volume-time yield (ethanol) at start of experiment	77.4 $g/l_{cat}/hr$	76.4 $g/l_{cat}/hr$	79.8 $g/l_{cat}/hr$

Table 2: A comparison of the properties of the three types of catalyst carriers used

Claims:

1. Catalyst / catalyst carrier with an aluminium content of less than 0.3 % by weight obtainable from mainly layer-lattice silicates which contain aluminium by a dealuminating process.

2. Catalyst / catalyst carrier according to claim 1, wherein the said catalyst / catalyst carrier has an aluminium content of less than 0.03 % by weight.

3. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said layer-lattice silicates used are smectite and / or have preferably montmorillonite structures.

4. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said catalyst carrier has a cumulative pore volume of between 0.2 and 0.9 ml/g.

5. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said catalyst / catalyst carrier has a total pore volume of between 0.6 and 0.7 ml/g.

6. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said catalyst / catalyst carrier has the shape of a spherical body.

7. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said catalyst / catalyst carrier has the shape of a ball.

8. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said catalyst / catalyst carrier has a diameter of between 1 and 10 mm.

9. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said catalyst / catalyst carrier has a diameter of between 4 and 6 mm.

10. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said catalyst / catalyst carrier has a pressure resistance of at least 10 N/mm.

11. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said catalyst / catalyst carrier has a pressure resistance of at least 20 N/mm.

12. Catalyst / catalyst carrier according to one of the proceeding claims, wherein said catalyst / catalyst carrier obtainable from lattice-layer silicates containing aluminium by carrying out the following steps:

- impregnating with an acid
- treating hydrothermally
- washing with an acidic, a basic or a neutral solution
- as well as optionally rinsing with water.

13. Catalyst / catalyst carrier according to claim 12, wherein said step

- of impregnating with an acid comprises impregnating with a mineral acid, in particular with phosphoric acid.

14. Catalyst / catalyst carrier according to one of the claims 12 to 13, wherein said step

- of hydrothermal treatment takes place at a temperature of between 160 and 300 °C and/or at an partial water vapour pressure of between 4 and 80 $bar_{abs.}$.

15. Catalyst / catalyst carrier according to one of the claims 12 to 14, wherein said step

- of hydrothermal treatment takes place at a temperature of between 220 and 260 °C and / or at an partial water vapour pressure of between 16 and 25 $bar_{abs.}$.

16. Catalyst / catalyst carrier according to one of the claims 12 to 15, wherein said step

- of hydrothermal treatment takes place completely or in part during the use of said catalyst / catalyst carrier in a hydration reaction.

17. Catalyst / catalyst carrier according to one of the claims 12 to 16, wherein said step

- of washing takes place at a temperature of between 20 and 100 °C.

18. Catalyst / catalyst carrier according to one of the claims 12 to 17, wherein said step

- of washing takes place at a temperature of between 70 and 90 °C.

19. Catalyst / catalyst carrier according to one of the claims 12 to 18, wherein said step

- of washing takes place with water, with hydrochloric acid or with water containing 0 to 30 parts of concentrated hydrochloric acid.

20. Catalyst / catalyst carrier according to one of the claims 12 to 19, wherein said step

- of rinsing takes place until the washing water becomes neutral.

21. Process for producing a catalyst / catalyst carrier according to one of the claims 1 to 11 by a process which comprises the steps according to the claims 12 to 20.

22. Process according to claim 21, wherein the catalyst / catalyst carrier is purified by burning off adhering organic carbon-containing compounds at a

temperature of between 300 and 1,000 °C, before the steps according to one of the claims 12 to 20 are applied.

23. Process of hydration of olefins, preferably C_2 or C_3 olefins, with water in the presence of at least one catalyst, which is made from a catalyst/catalyst carrier according to one of the claims 1 to 20 impregnated with acid.

24. Process according to claim 23, wherein the hydration reaction

- is carried out in a reactor
- an olefin to water molar ratio is adjusted to between 0.1 and 0.8 in the reactor
- has a gas hourly space velocity of 10 to 100 $l_n/min/l_{cat}$
- said catalyst contains 5 to 60 % by weight of acid, and
- the hydration reaction of the olefins is carried out at a temperature of between 160 and 300 °C and an pressure of between 20 and 200 $bar_{absolute}$.

25. Process according to one of the claims 23 to 24, wherein said acid with which the catalyst / catalyst carrier is impregnated is a 10 to 90 % by weight phosphoric acid.

26. Process according to claim 25, wherein said acid with which the catalyst / catalyst carrier is im-

pregnated is a 50 to 60 % by weight phosphoric acid.

27. Process according to one of the claims 23 to 26, wherein said catalyst contains 5 to 60 % of an acid, calculated as pure acid, in particular a mineral acid like phosphoric acid.

28. Process according to one of the claims 23 to 27, wherein the hydration reaction for producing ethanol from ethene is carried out at a temperature of between 220 and 260 °C and a pressure of between 60 and 80 bar.

29. Process according to one of the claims 23 to 28, wherein the olefin used and the water used are introduced into the reactor in gaseous form.

30. Process according to one of the claims 23 to 29, wherein said acid is introduced into the reactor during the course of the hydration reaction.

31. Process according to claim 30, wherein said acid used is phosphoric acid.

32. Process according to at least one of the claims 23 to 31, wherein said acid is injected into the reactor continuously.

33. Catalyst for the hydration of olefins to alcohols obtainable by bringing into contact the catalyst / catalyst carrier according to one of the claims 1 to 20 and the catalyst / catalyst carrier produced according to one of the claims 21 to 22 with a mineral acid, in particular phosphoric acid, respectively.

34. Catalyst for the hydration of olefins to alcohols according to claim 33 which contains 5 to 60 % by weight acid, calculated as pure acid.

35. Catalyst / catalyst carrier according to one of the claims 1 to 20, wherein the said catalyst / catalyst carrier has at least partly a cristobalite-like structure.

Summary

Dealuminated catalyst carrier, process for producing the catalyst carrier and process for hydrating C_2 or C_3 olefins with water in the presence of a catalyst which comprises this catalyst carrier impregnated with acid.

What is claimed is a dealuminated catalyst carrier, a process for producing a catalyst carrier with reduced aluminium content based on naturally occurring lattice-layer silicates, such as for example montmorillonite, as well as a process for the hydration reaction of C_2 or C_3 olefins in which said catalyst carrier with reduced aluminium content is used. For acid-catalysed hydration reaction the catalyst carrier is impregnated with phosphoric acid.

The improvements according to the invention of the hydration reaction compared to conventional processes include the fact that no aluminium is leached out of the carrier in the presence of the phosphoric acid. As a result no more blockage of the succeeding apparatusdue to aluminium phosphate are expected.

Figure 1:

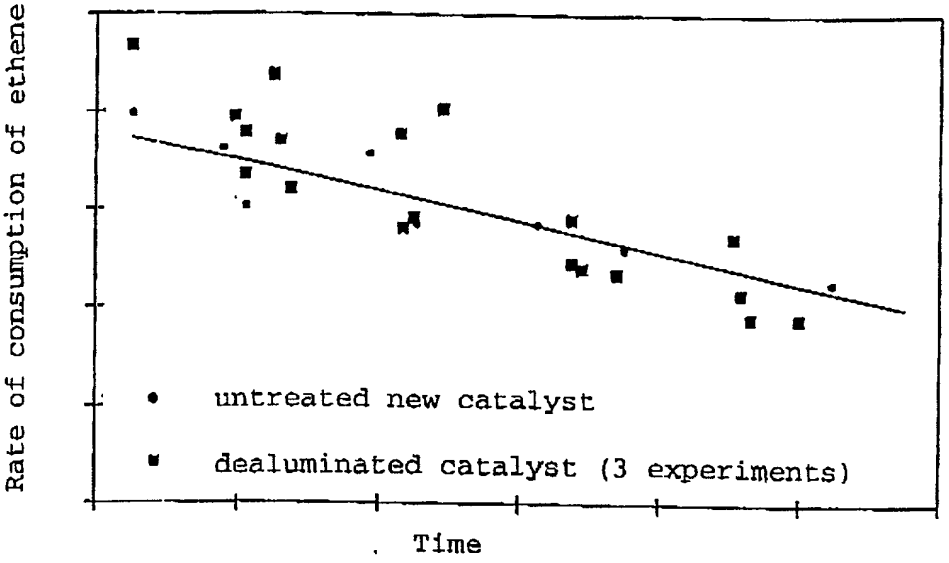
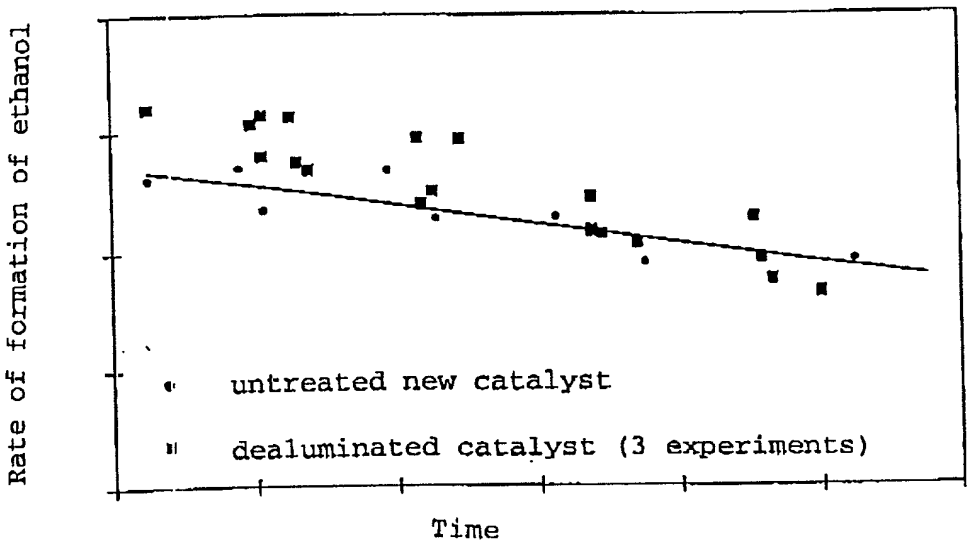


Figure 2:



CHECK PROPER BOX(ES) FOR ANY OF THE FOLLOWING ADDED PAGE(S) WHICH FORM A PART OF THIS DECLARATION

(x) Signature for third and subsequent joint inventors. Number of pages added __1__.

( ) Signature by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. Number of pages added _____.

( ) Signature for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR §1.47. Number of pages added _____.

* * *

( ) Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (CIP) application.

( ) Number of pages added _____

* * *

( ) Authorization of attorney(s) to accept and follow instructions from representative.

* * *

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( ) This declaration ends with this page

Attorney Docket No. Müller-22

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL, CONTINUATION OR CIP)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type: (check one applicable item below)

( ) original
( ) design
( ) supplemental

NOTE: If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application do not check next item; check appropriate one of last three items.

(x) national stage of PCT

NOTE: If one of the following 3 items apply then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR CIP.

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( ) continuation-in-part (CIP)

INVENTORSHIP IDENTIFICATION

WARNING: *If the inventors are each not the inventors of all the claims an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.*

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

DEALUMINIZED CATALYST SUPPORT, METHOD FOR PRODUCING SAID CATALYST SUPPORT AND METHOD FOR HYDRATING C_2- OR C_3-OLEFINS WITH WATER IN THE PRESENCE OF A CATALYST CONSISTING OF THIS CATALYST SUPPORT IMPREGNATED WITH ACID

SPECIFICATION IDENTIFICATION

the specification of which: (complete (a), (b) or (c))

(a) ( ) is attached hereto.

(b) (x) was filed on November 22, 2000, as (x) Serial No. 09/701,054 or ( ) Express Mail No., as Serial No. not yet known _____ and was amended on _____ (if applicable).

NOTE: Amendments filed after the original papers are deposited with the PTO which contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 C.F.R. §1.67.

(c) (x) was described and claimed in PCT International Application No. PCT/DE99/01898, filed on 1 July 1999, and as amended under PCT Article 19 on _____.

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

( ) In compliance with this duty there is attached an information disclosure statement. 37 CFR §1.97.

PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

(d) ( ) no such applications have been filed.

(e) (x) such applications have been filed as follows.

NOTE: Where item (e) is entered above and the International Application which designated the U.S. claimed priority check item (e), enter the details below and make the priority claim.

EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
Federal Republic of Germany	19829747.5	3 July 1998	Yes

ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

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_____

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POWER OF ATTORNEY

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number.)

C. James Bushman, Reg. No. 24,810; Loren G. Helmreich, Reg. No. 29,389; Carlos A. Torres, Reg. No 24,264; Marvin B. Eickenroht, Reg. No. 18,541; and Eugene N. Riddle, Reg. No. 18,541

( ) Attached as part of this declaration and power of attorney is the authorization of the above-named attorney(s) to accept and follow instructions from my representative(s).

SEND CORRESPONDENCE TO:

C. James Bushman
Browning Bushman
5718 Westheimer, Suite 1800
Houston, TX 77057

DIRECT TELEPHONE CALLS TO:
(Name and telephone number)

C. James Bushman
(713) 266-5593

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

Full name of **sole or first inventor**: Michael Sakuth

Inventor's signature: Michael Sakuth

Date: 01/05/01
(month/day/year)

Country of Citizenship: Federal Republic of Germany

Residence: Marl, Federal Republic of Germany DEX

Post office address: Lipper Weg 193
D-45772 Marl
Federal Republic of Germany

Full name of **second joint inventor**, if any: Gregor Lohrengel

Inventor's signature: Gregor Lohrengel

Date: 01/07/01
(month/day/year)

Country of Citizenship: Federal Republic of Germany

Residence: Dorsten, Federal Republic of Germany DEX

Post office address: Naheweg 3
D-46286 Dorsten
Federal Republic of Germany

ADDED PAGE TO COMBINED DECLARATION AND POWER OF ATTORNEY
FOR SIGNATURE BY THIRD AND SUBSEQUENT INVENTORS

300

Full name of **third joint inventor**, if any: Dietrich Maschmeyer

Inventor's signature: Dietrich Maschmeyer

Date: 01/19/01
(month/day/year)

Country of Citizenship: Federal Republic of Germany

Residence: Recklinghausen, Federal Republic of Germany DEX

Post office address: Wickingstrasse 9a
D-45657 Recklinghausen
Federal Republic of Germany

400

Full name of **fourth joint inventor**, if any: Guido Stochniol

Inventor's signature: Guido Stochniol

Date: 01/26/01
(month/day/year)

Country of Citizenship: Federal Republic of Germany

Residence: Marl, Federal Republic of Germany DEX

Post office address: Langehegge 174
D-45770 Marl
Federal Republic of Germany

Full name of **fifth joint inventor**, if any:

Inventor's signature: _____

Date: _____
(month/day/year)

Country of Citizenship:

Residence:

Post office address:

Full name of **sixth joint inventor**, if any:

Inventor's signature: _____

Date: _____
(month/day/year)

Country of Citizenship:

Residence:

Post office address: